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1. Designation of the matter:
   Patent application No. 151347 (1975)
2. Title of the invention: MULTICOLOR INK JET RECORDING PAPER
3. Applicant for amendment (Patent applicant)
   Jujo Paper Company, Ltd.
4. Representative: Patent attorney: Ichikawa Rikichi et al., Tokyo, Japan
5. Object of amendment: The whole specification
6. Contents of the amendment: As per attached sheets
7. Inventor and representative other than the above:
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   (2) Representative: Patent attorney: Endo Tatsuya, Tokyo, Japan

Amended specification

1. TITLE OF THE INVENTION: INK JET RECORDING PAPER

2. CLAIM:

Ink jet recording paper characterized in that the ratio of air resistance (sec.) to basis weight (g/m^2) is not more than 0.3, and besides when 0.004 ml of water base ink for ink jet recording is dropped, the time of absorption of ink falls within not less than 2 seconds to not more than 60 seconds.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to recording paper suitable for ink jet recording using a plurality of ink jet elements, multicolor ink jet recording in particular, and provides ink jet recording paper where ink adhered to the surface of paper is absorbed inside the paper layer quickly, and even in the case that different colored ink drops are overlaid on and adhere to the same location on the surface of paper in a short time, the phenomenon such as outflow or blur can be avoided, and furthermore, the spread of ink dots on the surface of paper can be restricted to the degree where the clearness of images

is not impaired.

The ink jet recording system using ink jet elements is a recording system characterized in that the system virtually eliminates the occurrence of noise and besides while it allows high-speed recording, multicolor recording can be easily performed on ordinary plain paper, and the system has developed remarkably in recent years.

In the meantime, while it is necessary that ink jet recording paper has a characteristic that the ink drops adhered on said surface of paper are quickly absorbed into the interior of the paper layer and thus the ink becomes dry by appearances and at the same time a characteristic that the spread of ink dots on said surface of paper is restricted, and in the case that ink jet recording in mono color is performed on commercially available high to medium quality of paper using one ink jet element at a relatively low speed, these two opposite characteristics can be satisfied because sufficient time can be spared for absorption of ink and at the same time ink drops are rarely overlaid. Namely, in this case, if ink drops adhered on the surface of paper are absorbed inside the paper within several seconds to dozens of seconds, the fade of ink dots can be comparatively easily controlled to satisfy the degree required without causing much inconvenience for handling of recorded paper.

However, in the case that multicolor recording is performed or high-speed ink jet recording is conducted by jetting different colored ink in two or more colors to one point on the paper and by adhering it thereon using two or more ink jet elements simultaneously, the first ink drop that adheres to the surface of the paper is overlaid with other ink drop that adheres to the surface of the paper afterwards, or different colored ink drops, which adhere to the surface of the paper almost at the same time, are overlaid with each other, unless the ink drops are absorbed into the interior of the paper layer rapidly, and thereby trouble may occur in that ink outflows from the paper saturated with ink, or the ink remaining on the surface of the paper may cause stains while handling the recorded paper.

Therefore, though paper having a specially good ink absorption property is required for multicolor ink jet recording or single color high-speed ink jet recording, the paper having a good absorption property has generally shortcomings in that the spread of ink dots on the surface of the paper is large, and the resolution of recorded images lowers, and thus it is the actual situation that recording paper that possesses all of the requirements as desired by businesses involved is not available.

The present invention is to provide ink jet recording paper that is suitable for ink jet recording using water base ink as included in the claim, namely, the paper having a property to rapidly absorb water base ink drops into the interior of the paper and

additionally having a property that the spread of ink dots on the surface of paper is small.

In order to increase the capacity of absorption of ink with paper having a constant basis weight, the methods that increase the porosity of the interior of the paper by increased bulkiness or by adding of porous materials having a high ink absorption property into the interior can be generally considered.

In the case of paper having a basis weight of 64 g/m^2 and an apparent density of 0.7, its absorption capacity of ink indicates that 55% of the volume of the paper layer is its porosity since the true specific gravity of ordinary wood pulp is approx. 1.55. Assume three granular ink drops 70 μ in dia. adhere to the inside of a circle 200 μ in dia. on said paper, the ratio of the volume of adhered ink and the cavity of the inside of the paper layer is approx. 1:3, which indicates that the paper still keeps a fairly large absorption capacity. Though the large bulkiness of paper or large porosity is preferable as indicated above as far as the ink absorption capacity is concerned, this is not the decisive factor.

As a result that the present inventors studied strenuously the relation between the absorption property of ink drops into paper layers and the characteristics of paper, it is revealed that in the case of paper made of the same paper materials, the larger the apparent density of paper, the larger the diameter of ink dots. (See Table 1.) While the density of paper can be varied not only by the pressure calendering of paper-making sheets but also by the kind of wood pulp or raw materials, beating, and addition of fillers, the diameter of ink dots is affected by any of these conditions. These phenomena indicate that the absorption of ink is affected by the profile of cavity in the paper layer, or its diameter in particular.

With beating continuing, the apparent density of paper will increase in accordance with the fibrilation of fibers, whereas when fillers are added, the bulkiness of paper tends to increase due to the reduction in bonding between fibers, and therefore the rate of porosity and the degree of air resistance that relates directly to the average hole diameters are more suitable for use as an index of ink absorption.

Experiment 1 shows the results of measurement of the relation between the degree of air resistance and the diameter of ink dots with density changed by making paper from three kinds of basis weight from paper stock in a fixed ratio of blending and by defining the number of calender nips.

Experiment 1.

As pulp materials, LBKP and NBKP were blended at the ratio of 1:1, and beat

in a refiner to freeness (C.S.F.) 400 ml, to which 0.5% of Kaimen (polyamid epichlorhydrine modified resin) and 30% of precipitated calcium carbonate were added, and three kinds of paper-making base paper having a basis weight of 40g, 65g, and 81g each were manufactured by using a long net type paper making machine.

A 5% aqueous solution of a mixture of oxidized starch and PVA at the ratio of 1:1 was coated as a surface sizing solution on the three kinds of paper-making base paper in different basis weight at the rate of application quantity of 2 g/m^2 using a size press system, and after drying, machine calendering finish was applied and paper (A) - (K) is yielded.

Using the paper having a density of 0.53- 0.89 as produced above, ink in three colors, cyan, yellow and magenta, was jet sprayed from each of three ink jet guns having a nozzle diameter of 40 μ. Table 1 shows the results of measurement of the size of dot diameters (average values of three colors) taken from the recording of the diameter of printing particles.

Table 1

Kind of paper	No. of calender nipples at time of calender finishing	Basis weight (g/m^2)	Apparent density (g/?)	Degree of air resistance (sec.)	Degree of air resistance/basis weight	Dot dia. (Average value of 3 colors) (μ)
A	0	65	0.53	4	0.06	215
B	1	65	0.66	8	0.12	228
C	3	65	0.70	11	0.17	238
D	5	65	0.74	17	0.26	242
E	7	65	0.80	22	0.34	257
F	9	65	0.89	40	0.61	264
G	1	40.	0.58	3	0.08	223
H	7	40	0.75	14	0.35	255
I	1	81	0.54	8	0.10	220
J	5	81	0.71	17	0.21	237
K	9	81	0.82	76	0.93	258

According to the result of the experiment of ink jet recording, when the diameter of ink dots is 250 μ or more with the diameter of ink particles at 75 μ, sharpness becomes insufficient considerably, and thus if it can be preferably limited to 235 μ or less, nearly satisfying sharpness is achieved. In the meantime, since air resistance varies depending on basis weight, it is proved from the table that the ratio of air resistance to basis weight at 0.3 or less, preferably 0.15 or less, is best suitable for multicolor ink jet recording paper in particular. In this case, though it is desired that the density of paper is 0.7 g/cc or less, the density other than this range can be used for mono color printing due to the reasons stated below.

As conditions of raw materials for manufacturing of such paper, it is necessary to maintain the freeness (C.S.F.) at 200 ml or more, preferably at 300 ml or more so as not to create a closely bonded fiber construction without furthering of beating of raw pulp materials.

Also, the fillers themselves are fine as described below, and in view of the fact that the fillers fill cavities and reduce the hole diameter, it can be considered that fillers affect the spread of ink dots adversely, whereas as a result that fibers are prevented from bonding due to the addition of fillers, the bulkiness of paper is increased, and thus cavities tend to give an favorable effect on the spread of ink dots, accompanied by an excellent ink absorption property of fillers.

While fillers used for such a purpose include heavy calcium carbonate, precipitated calcium carbonate, silica, aluminum hydroxide, titanium oxide, urea-formalin resin group organic fillers in addition to routinely used clay, talc, and others, paper-making base paper internally added with precipitated calcium carbonate, silica particles, or organic fillers in particular, becomes bulky, and thereby the ink absorption property so improves that these fillers are suitable for manufacture of paper as intended by the present invention.

These fillers are added to the raw material before paper making, and the effect of the present invention is clearly shown by setting the ratio of addition of these fillers at 10% or more, preferably 20%, to the basis weight of pulp.

Now, in the case of paper used for high-speed or multicolor ink jet recording which is the purpose of the present invention, unless the paper has a good ink absorption property wherein Steckigt sizing degree (a 60 g/m^2 standard based on JIS P-8122) is restricted to not more than 3 sec., preferably not more than 1 sec., the phenomena like stains caused by wet ink on the surface of the recording paper, or outflowing due to the overlaid condition of ink drops occur at the time of ink jet recording, and thus clear recording images cannot be produced.

Presently, inventors have taken notice that even in the case of paper of low size degree like the Steckigt sizing degree being practically 0 sec., the ink absorption property can be expressed by measuring the amount of time (sec.) from the time when ink is dropped on the surface of the paper with a needle of a syringe based on the newsprint oil absorption testing method JIS P-8001 to the time when the ink is absorbed in the surface of the paper, and they have found that the property of paper, which is suitable for ink jet recording, preferably for multicolor application in particular, is specified using such amount of absorption time.

Experiment 2 shows the dot diameters and the state of the outflow of ink at the

location where the ink in different colors are overlaid when the absorption time of ink is controlled by changing the degree of sizing on the surface.

EXPERIMENT 2

Table 2 shows the result of the observation on the size of dots and the outflow of ink when water base ink 0.004 ml was dropped on the surface of paper (L) - (T) using a syringe needle. The paper-making base paper as well as the surface sizing conditions of paper (L) - (T) is different, and the absorption time of ink, which indicates the time until ink is absorbed in the surface of paper, and the recording of the diameter of printing dots 75 μ were observed using the same method of experiment 1.

(S-M in the table stands for styrene - maleic acid copolymers.)

Manufacturing conditions of paper-making base paper

Paper (L) - (S)

As raw material pulp, LBKP and NBKP were blended at the ratio of 1:1, and were beat in a refiner to freeness (C.S.F.) 400 ml, to which 0.5% of Kaimen (polyamid epichlorhydrine modified resin) and 30% of precipitated calcium carbonate were added, and base paper having a basis weight of 65g was manufactured by using a long net type paper making machine.

Paper (T)

As raw material pulp, LBKP and NBKP were blended at the ratio of 1:1, and were beat in a refiner to freeness (C.S.F.) 400 ml, to which 0.5% (to pulp) of Kaimen (polyamid epichlorhydrine modified resin), 30% (to pulp) of precipitated calcium carbonate, and 2% (to pulp) of aluminum sulfate were added, and base paper having a basis weight of 65g/m^2 was manufactured by using a long net type paper making machine.

Sizing conditions of the surface of paper (M) - (T)

Five percent water solutions of a mixture consisting of oxidized starch and PVA or oxidized starch, PVA and styrene - maleic acid copolymers were coated at the rate of application quantity of 2 g/m^2 as surface sizing fluids using a size press system, and dried.

Table 2

Kind of paper	Ratio of components of surface sizing solution Oxidized starch : PVA : S-M	Steckigt sizing (sec.)	Absorption time of ink (sec.)	Dot dia. (μ)	State of ink outflow
L	Without surface sizing	0	0.8	298	None
M	1:1:0	0	2.2	208	None
N	1:1:0.01	0	4	200	Nearly none
O	1:1:0.02	0	8	211	Nearly none
P	1:1:0.04	0	12	217	Nearly none
Q	1:1:0.08	0	20	205	Fairly large
R	1:1:0.1	2	56	194	Fairly large
S	1:1:0.2	5	128	201	Large
T	1:1:0.2	20	>300	187	Very large

Table 2 shows that in view of the size of dot diameters and the state of ink outflow, the degree of sizing is required to stay within 0 - 3 sec. for multicolor ink jet recording paper, and moreover, when it is reviewed in terms of ink absorption time more precisely, it is preferable to fall within approx. 2 sec. - 60 sec.

So called microscopic sizing paper having its ink absorption time falling within the stipulation as defined in the present invention is manufactured by coating paper-making base paper using a sizing press with water soluble polymers such as oxidized starch, PVA, galactomannan gum, alginic acid soda, CMC, other cellulose derivatives, casein, soybean protein, or polyacrylamide, which are mostly used for base paper obtained by adding wet paper strengthening agents, added with sizing agents, hydrophobic material, or synthetic resin latex that contains as a main ingredient rosin and its derivatives, petroleum resin, phtalic acid, maleic acid and its derivatives, wax, synthetic resin fatty acid, or alkyl ketene dimer, if needed, and besides further blended with pigments and fillers such as kaolin, calcium carbonate, aluminum hydroxide, satin white, titanium oxide, or urea-formalin group organic fillers together with its dispersants, if needed, in place of fillers for wood pulp within the freeness as mentioned before, sizing agents mostly used because of the reason mentioned later, and size fixing agents.

When coating paper with water base paint using a sizing press, infiltration or penetration of paint is controlled in coating process by providing base paper with the degree of sizing in advance using an appropriate sizing agent, thereby preventing paper cutting caused by lowered paper strength and migration of paint into the interior of paper layers due to absorption of excessive paint, however, the adding of sizing agents into the interior is not allowed for the case of the present invention due to the reason mentioned as above, and therefore it is preferable to add wet paper strengthening agents in the preparation process of paper-making raw materials of base paper so as to prevent

lowering of paper strength at the time of coating.

It is desirable that wet paper strengthening agents do not lower the ink absorption property of paper itself, but improve wet strength, for example; available for use are polyamide resin, its epichrohydrin modified resin or ethoxyl modified resin in particular, gluocisal, melamine resin and its modified resin, urea resin and its modified resin, polyethylene amine and its derivatives, dialdehyde starch or dialdehyde gum.

Also, when paper-making base paper is manufactured, use of sizing fixing agents such as aluminum sulfate helps prompt the sizing effect of the above sizing agents, but its use should be avoided as they may cause discoloration of ink or coagulation depending on the situation.

(Therefore, the appropriate range of PH of paper-making raw materials is 5 - 10 except in the case of adding of aluminum sulfate which PH is 5 or less as generally observed.)

When paint contains pigment or fillers, it is desirable in this case that the required quantity of application to the recording surface is 0.5 g/m^2 or more, preferably 1 g/m^2 or more as the above water soluble polymer binder, and the coating of the recording surface is 5 g/m^2 or more, preferably 8 g/m^2 or more, as a solid portion.

In the case of impregnation coating on both surfaces using a sizing press, double the above figures is required. Although these figures are regarded as difficult for coating with an ordinary sizing press, it can be realized easily by the method disclosed by the present invention since the degree of sizing is practically 0 sec.

It should be noted that a large quantity of coating can properly control the spread of ink dots and it also can uniformly make the profile of the spread as close as a circle, and thereby the clearness of ink jet recording can be provided by this condition together with the internal addition of fillers as described before.

Moreover, when coating is applied to base paper which size degree is practically 0 sec., there are a lot of advantages in that as a result that the migration of binders are accelerated, ink is absorbed well and drying is prompted in spite of a large quantity of application.

Therefore, it does not conform to the purpose of the present invention to coat the base paper that is once applied with surface sizing using a size press like ordinary coated paper for example, since the absorption of ink is prevented.

However, base paper coated directly with paint containing pigment using coaters other than size presses, for example, such as roll coaters, air knife coaters, blade coaters and the like, is suitable for mono color ink jet recording paper.

Examples of manufacture of ink jet recording paper and its performance of the

present invention will now be described with reference to the embodiments as stated below:

EMBODIMENT 1

From pulp raw materials of 100 parts of LBKP with 400 ml freeness (C.S.F.) blended with 10 parts of first class China clay, and 0.3 parts of Kaimen 557 (make of Dicks Herculeus) as an yield improvement agent plus wet paper strengthening agent, base paper having a basis weight of 57 g/m^2 was manufactured using a small long net testing paper making machine and the base paper was coated with a 5% water soluble solution of a mixture of oxidized starch and PVA mixed at the ratio of 1:1 using a size press system, and thereby surface coated paper was yielded. The absorption time of water base ink for ink jet recording (viscosity: 1.8 c.p., surface tension: 45 dyne/cm) on the surface coated paper was 6 sec.

Ink in three colors, cyan, yellow and magenta, was jetted on the surface coated paper thus yielded as recording paper, from three ink jet guns with a nozzle having a caliber of 40 μ almost at the same time for recording of printing dots 65 μ in dia. and the result of recording is shown in Table 3 wherein the above result is compared with printing on paper-making base paper, high-quality paper available on the market, and newsprint, which were used as recording paper.

Table 3

Kind of recording paper	Basis weight (g/m^2)	Density (g/cc)	Penetr-ability (sec.)	Penetr-ability/ Basis weight	Steckigt size (sec.)	Ink absorption time (sec.)	Dot dia. (μ)	State of ink outflow
High-quality paper available on the market	64	0.78	16	0.25	21	>300	130	Large
Newsprint	54	0.62	22	0.41	0	31	260	Small
Paper-making base paper	57	0.53	6	0.10	0	1	250	None
Paper used for the present embodiment	60	0.55	8	0.13	0	6	180	None

Though high-quality paper available on the market as shown as an example for comparison has the ratio of penetrability to basis weight of 0.25, clear recording does not result. This is because due to the large absorption time of ink, the absorption and drying of ink drops are slow and the outflow of ink at the ink overlaid area on the

surface of paper occurs. In the case of newsprint, though its ink absorption time is appropriate, the dot diameter gets larger due to a comparatively large ratio of penetrability to basis weight, and thus a clear image quality cannot be obtained, and besides, when the paper-making base paper, which was manufactured as in this embodiment, is used as recording paper without any change, the absorption time of ink is small with a larger dot diameter, and thus a low quality of image is recorded.

In the meantime, when recording paper as obtained in this embodiment was used, wherein both penetrability and ink absorption time fall in the range as specified in the claim, the spread of the dot diameter was almost equivalent to high-quality paper, and also the outflow of ink did not occur at all.

EMBODIMENT 2

The paper-making base paper I same as used in embodiment 1 was coated with an aqueous solution of 7% density containing ingredients at the ratio of oxidized starch 6, PVA 2, and styrene-maleic acid copolymer-ammonium salt 1 using a size press system, and surface coated paper with penetrability 7 sec. and ink absorption time 40 sec. was yielded. As a result that three color ink jet recording was conducted under the conditions same as in embodiment 1, the dot diameter could be restricted to 170 μ and the outflow of ink from the overlaid ink area hardly occurred.

EMBODIMENT 3

In place of the surface sizing solution used at embodiment 2, an aqueous solution of 30% density containing ingredients at the ratio of 0.2 parts of hexametaphosphoric acid soda as a dispersant, 10 parts of oxidized starch as a binder, 10 parts of PVA, 2 parts of styrene-butadiene latex, and 0.6 parts of calcium stearate as a releasing agent, blended with 100 parts of kaolin, was coated at an application quantity of 10 g/m^2 using a size press system, and surface coated paper with penetrability 15 sec. and ink absorption time 30 sec. was yielded.

As a result that three color ink jet recording was performed, the diameter of the dot was 190 μ and the outflow of ink from the overlaid ink area hardly occurred.

EMBODIMENT 4

Pulp raw materials of 80% by weight of LBKP with 400 ml freeness (C.S.F.) blended with 20% by weight to the pulp of NBKP with 450 ml freeness (C.S.F.) were internally added with 25 parts by weight of precipitated calcium carbonate as fillers, and 0.2 parts by weight of Kaimen 557 (make of Dicks Herculeus, registered mark) as an

yield improvement agent plus wet paper strengthening agent, respective parts being the ratio to the pulp solid component, and paper was manufactured at 60 g/m^2 basis weight using the paper-making machine same as used in embodiment 1, and paper-making base paper was obtained.

Using an air knife coater, one side of the base paper was applied with paint consisting of a solution having a density of 25% of solid ingredients of blending components consisting of 100 parts of precipitated calcium carbonate, 10 parts of oxidized starch, 5 parts of SBR latex, a small quantity of hexametaphosphate soda as a dispersant, and a small quantity of stearic acid calcium as a releasing agent, and surface coated paper with 12 g/m^2 of coated solid component quantity as well as with 0.5 sec. of Steckigt sizing degree was obtained.

The dot diameter resulting from the printing recording on the surface coated paper thus obtained using an ink jet gun with black water base ink having a viscosity of 5 c.p. showed a circle similar to the circle recorded on surface coated paper available on the market, and the time required for drying of these ink drops was within 10 sec.

However, with paper-making base paper coated with 4% oxidized starch solutions using a sizing press, the base paper was applied with paint consisting of the same solution as above, and it took not less than 30 sec. to dry the ink drops of printing recording on the surface coated paper with 9 g/m^2 of coated solid component quantity and with 0 sec. of Steckigt sizing degree using an ink jet gun same as above.

EMBODIMENT 5

Using an air knife coater, one side of paper-making base paper same as used in embodiment 4 was applied with paint consisting of a solution having a density of 30% of solid ingredients blended at the ratio of 80 parts of kaolin as a pigment, 20 parts of precipitated calcium carbonate, 0.2 parts of hexametaphosphate soda as a dispersant, 0.2 parts of polyacrylic acid soda, 12 parts of oxidized starch as a binder, 12 parts of PVA and 0.6 parts of stearic acid calcium as a releasing agent, and surface coated paper with 11 g/m^2 of coated solid component application quantity and with 0 sec. of Steckigt sizing degree was obtained.

Recording was performed on the surface coated paper under the condition same as in embodiment 4 with an ink jet gun, and as a result, both the dot diameter and the time for drying of ink drops showed a good printing recording almost as good as the result on the surface coated paper of embodiment 4.

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